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CHLORINATION ASSESSMENT PROCEDURES

PREPARED FOR

Working Group II
of the Water Management
Steering Committee

Ministry of the Environment
Ontario

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NOTE

The receiving water assessment techniques presented in this report describe the methods commonly in use within the Ministry. Alternative techniques exist and/or will eventually be developed. Consultation with Ministry of the Environment staff is advisable to determine the suitability of the alternative techniques.

Reference to equipment brand names or suppliers in this report is not to be interpreted as an endorsement by the contributing authors, or by the Ministry of the Environment.

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INTRODUCTION

Chlorination was introduced at the turn of the Century to deodorize and disinfect sewage. As a result, there was a decrease in the number of outbreaks of common waterborne infections. In order to uniformly implement chlorination, the MOE adopted the following policy: "The chlorine residual in the contact chamber discharge should be maintained at 0.5 mg/L during periods that require chlorination.". Year round chlorination is required at all mechanical plants except in cases where there is no existing or potential impairment of water quality or water use. If a case can be established to support exemptions from chlorination then this would apply for the winter months November 15 to May 15 only. Lagoon effluents generally do not require disinfection due to the long retention times before discharge. However, disinfection of the effluent will be required where a water use may be impaired by a lagoon discharge (e.g. water supply or bathing beach).

This chlorination practice has been accepted and continues to be used; however, concerns as to the toxicity of chlorine have been raised and have led to the MOE endorsement of the 0.002 mg/L chlorine residual Provincial Water Quality Objective for the protection of aquatic life.

The MOE chlorination policy is presently under review. The draft of the revised disinfection policy (Draft #3) has been circulated to the regions for comments.

OPERATIONAL CONSIDERATIONS WITH CHLORINATED EFFLUENTS

1. Many of the STPs use the orthotolidine method to measure the residual chlorine levels. This method is generally inaccurate and as a result more chlorine is used than that required with a more accurate measuring method (for example amperometric or DPD techniques).

2. Many STP operators tend to be unconcerned about the accurate use and maintenance of the test equipment which reduces the precision of the test.

3. Some plant operators consider the 0.5 mg/L chlorine level as a minimum, not an optimum level requirement, and tend to exceed the guideline (i.e. over-chlorinate).

4. STPs are subject to overloading and breakdowns which make the chlorination practice haphazard. Batch over chlorination or insufficient chlorination may occur.

5. Some plants use automated chlorine application. These devices add chlorine based on TRC measurements taken throughout the day. Other plants use manual application which can be more of a hit or miss operation.

6. Urban storm water runoff, agricultural runoff and some industrial discharges (e.g. from food processing plants or abattoirs) are not chlorinated and usually carry high levels of bacteria and other contaminants.

PROBLEMS WITH THE USE OF CHLORINE

1. The chlorine residual in receiving waters has been shown to be exceedingly toxic to aquatic life (Brungs, 1973). It has also been shown that fish will avoid chlorine concentrations of .01 and 1.0 mg/L, but are attracted to chlorine concentrations of 0.1 mg/L which is an intermediate lethal level (Sprague, 1969).

2. Chlorine can combine with organics in the sewage effluent to produce a variety of potentially carcinogenic organohalide compounds (EPA, 1975).

3. Pathogenic and indicator organisms have been shown to regrow back to approximately original levels after chlorination (Shuval, 1973). MOE staff are currently studying the phenomenon of regrowth of pathogens discharged in STP effluents. The study will include both summer and winter effluent sampling with and without chlorination.

4. Viruses tend to be more resistant to chlorine than bacteria and water can serve as a vector for some human viruses such as hepatitis (Craun, 1976).

5. Many of the STPs are placed on receivers that have insufficient flow to properly dilute the chlorinated effluents. Hence, in insufficient receivers, discharges containing chlorine require large mixing zones before the Provincial Water Quality Objective for chlorine can be met.

CHLORINE TOXICITY

A) Although chlorine is very toxic to fish the Ministry of the Environment has only documented seven fish kills specifically caused by the discharge of chlorine into streams.

Two fish kills were a result of sewage treatment plants dosing the effluent with higher than normal concentrations of chlorine. One kill was the result of the incorporation of a new chlorine contact chamber at a sewage treatment plant. Two fish kills were the result of swimming pools being emptied when they contained high concentrations of chlorinated cleaner. One kill resulted from a discharge from a hatchery tank after sterilization, and another incident was a kill brought about by trout poachers using chlorine.

However, this evidence may fall short of defining the total ecological impact of chlorine discharges because some incidences of chlorine toxicity are unnoticed, or unreported or the Ministry officials arrive too late to definitely relate the fish kill to chlorine. By the time the fish kill is apparent it may

be too late to definitely link the kill to chlorine, unless the presence of chlorine is evident in the receiver and/or effluent discharge.

B) The objective at sewage treatment plants is to chlorinate to a point where the total residual chlorine of the final effluent is 0.5 mg/L. To go from this 0.5 mg/L concentration to the stream and lake criteria of 0.002 mg/L, a reduction factor or dilution factor of 250 to 1 is required assuming instantaneous complete mixing of effluent with receiving waters. When an effluent is discharged so as to create a mixing zone, the dilution factor of 250:1 should be met along an acceptable boundary of the mixing zone, although the concentrations of chlorine within the mixing zone are allowed to exceed the Provincial Water Quality Objectives (PWQO). A recent assessment of streams in the MOE Central Region revealed that under conditions of low streamflow, only 2 out of 32 plants which discharge continuously to streams in the Toronto area have sufficient dilution (based on the complete mixing assumption).

A study by Wisz, Ellis and Inniss (1978) indicated that chlorine decay rates in receiving waters were highly variable and dependent on differences in stream morphology, dilution ratios, and chemical and physical processes. Thus any mixing zone definition or chlorine assessment studies require laborious and expensive field investigations.

A number of field impact studies have been carried out in areas where the chlorine Objective of 0.002 mg/L was exceeded. In general, these impact studies have not clearly demonstrated chlorine toxicity.

EFFECTS OF CHLORINE

This paper will not deal with the chemistry of chlorine reactions (Chambers, 1971), the efficacy of chlorine as a disinfectant (EPA, 1975), or the environmental aspects of chlorination (Ellis, 1976) since these topics are well documented in the literature.

ASSESSMENT TECHNIQUES

A) Analytical Methods

It appears that new techniques and instruments are on the horizon but at present it is very unlikely that any of the instruments that are portable can accurately measure to .002 mg/L chlorine using a river sample and the accompanying interference constituents.

At present, the colorimetric DPD comparator or spectrophotometer techniques are only accurate to about 0.05 mg/L. The DPD method (Nessler comparator) is simple to use, yet would be sufficiently accurate for the STP operator to measure chlorine in effluents at the point of discharge. Commercially available amperometric units are probably accurate to about .02 or even 0.01 mg/L - still not sufficient for an objective of 0.002 mg/L. The Fisher-Porter unit is probably the best portable amperometric unit for field work. However, it does require a well-trained technician to operate, as well as a constant power supply which could be a problem in field situations.

There was a new portable unit manufactured by N-CON Ltd., supposedly accurate to 0.001 mg/L. However, N-CON removed this unit from the market before the MOE had a chance to test it. A similar unit has been developed by NBS but has not yet surfaced as a viable commercially available instrument.

An outline of some of the residual chlorine measurement techniques has been produced by S. F. Wisz (1978).

B) Sample Collection

Samples for residual chlorine should be collected in 1 litre glass bottles which had been previously "aged" overnight in tap water and rinsed with deionized distilled water, to ensure that residual chlorine will not be adsorbed onto the walls of the sample container. Analyses for residual chlorine should be ideally performed on site and temperature should also be recorded with each sample run. Stream flows and STP flow records should also be obtained or measured for the sampling period.

C) Field Survey Procedures

1. Rivers

Field Survey Procedures are described by Gowda (1980b), and are summarized below:

The field surveys are designed to collect data on: outfall discharge and background water quality characteristics, and on the transverse distribution of chlorine at four to six transects. The details of field surveys are usually dependent on site-specific conditions; however, a general field study procedure is described below.

The location of transects can be based on preliminary *in situ* measurements of a conservative parameter (e.g. conductivity) at selected access points to establish the approximate longitudinal boundary of the mixing zone. The selected locations of transects should be marked on a map so that they can be readily identified in the field during further surveys. Cross-sectional depths must be measured at a minimum of 15 points at known lateral distances measured from a reference bank (usually the outfall bank). Velocity measurements must also be taken at least at two transects using standard streamflow gauging procedures; however, measurements at all transects are desirable. (Note: At transects where velocities are not measured, the Manning's equation can be used to simulate the velocity profiles using measured depth profiles.)

Water samples must be collected at the upstream boundary and at the effluent outfall, and at each point where cross-sectional depths and velocities are measured. The samples can be collected at selected points at each transect (viz., less points outside effluent plume, alternate points, etc.) to reduce sample analysis costs, in which case the concentrations at other points are obtained by interpolation during data analysis. In order to account for the possible effects of fluctuations in effluent water quality and discharge on the instream concentrations, the sampling is carried out either by following the same plug of water beginning at the

outfall and proceeding to successive downstream transects, or during a round-the-clock intensive survey when samples are collected at each point at 3 to 4 hr. intervals. Obviously, the selection of a sampling methodology would depend on the man-power, time and other resource constraints, as well as the objectives of the study.

In some cases, it may be desirable to inject a solution of dye continuously to gather data on the transverse distribution characteristics of the river. This is particularly useful to simulate effluent discharge from proposed outfall locations, and in cases where relocation of an existing outfall is being considered. The dye injection must be maintained for 2 to 3 hours or more to establish steady state conditions. The cross-sectional distributions of dye at selected transects can be obtained directly through fluorometric tracing; however, in shallow rivers where the passage of a boat is difficult, it will be necessary to collect water samples at known cross-sectional points for dye concentration analysis.

Generally, two surveys are carried out under different instream hydraulic conditions so that the data of one survey can be used to calibrate the model, which is then verified using the data of the second survey. If man-power and other resource constraints are limited, then the data of one survey may be used to validate the model. The limitations of the latter approach must be given due consideration in using the predictions of the model for planning and management purposes.

2. Lakes

Concise, well illustrated procedures for modelling initial mixing and surface dilution are described in the MOE reports: Dispersion of Effluent Plumes for Diffusers and Near Shore Regions of the Great Lakes. Volume I. Initial Mixing Processes by Y. Hamdy, 1981 and Volume II, Surface Dilution by B. Kohli. 1981. A very brief summary of the information required to describe the mixing zone in a lake is as follows:

1. outfall characteristics and design
2. concentration of chlorine in the effluent

3. current direction and magnitude
4. topography of the lake bottom
5. seasonal temperature of the water - to calculate the chlorine decay rate

D. Prediction Techniques (Rivers)

1. One Dimensional Model.

This model is applicable to river situations where the effluent is instantaneously mixed with the entire river (i.e. the instantaneous complete mixing assumption is valid). This method was used to predict the concentrations of chlorine below the Brantford waste water treatment plant outfall (Post and Gowda, 1980). The average concentration in the river is determined from:

$$C_a = \frac{(C_e)(Q_e)}{Q_r}$$

C_a = completely mixed concentration of pollutant in river just below outfall
C_e = concentration of pollutant in effluent
Q_e = effluent flow rate
Q_r = total river flow rate, given by the sum of upstream and effluent flow rates

A modified form of the above relationship can be used to determine the chlorine effluent concentration that will meet the Provincial Water Quality Objective (PWQO) after mixing.

$$C_{eA} = \frac{Q_r C_s}{Q_e}$$

C_{eA} = allowable effluent concentration to meet PWQO
Q_r = total river flow rate, given by the sum of upstream and effluent flow rates
C_s = Provincial Water Quality Objective for residual chlorine
Q_e = effluent flow rate

Post & Gowda (1980) outline how to calculate the concentration of chlorine immediately below the Brantford outfall using various design criteria. They used the following relationships to calculate the downstream distance, X_s, where the chlorine concentration is equivalent to the PWQO:

$$C_s = C_a \exp(-KX_s/U_{av})$$

$$X_s = \frac{U_{av}}{K} \log_e (C_a/C_s)$$

U_{av} = average velocity of streamflow
K = decay rate of residual chlorine in the river

2. Mixing Zone Models (Two Dimensional Model)

There are models for which nomographs as well as computer programs are available. The nomographs should be used when a stream stretch can be described by an average width, an average depth and an average velocity (Gowda, 1981). Generally the nomogram is best suited for preliminary analysis; otherwise the computer analysis is recommended. The following are brief descriptions of computer models (Gowda, 1981):

MIXANDT - Applied to data analysis, this program requires as input: (i) cross-sectional sampling data for conservative and/or non-conservative parameters; (ii) cross-sectional depths; (iii) velocity profiles (optional). The program output includes mass flux of non-conservatives (required to determine decay rates), variance for estimation of dispersion coefficient, and cross-sectional concentration distributions, expressed nondimensionally. The latter output can be used for comparison with model predictions, during calibration and verification studies.

MIXCALBN - A water quality prediction model suitable for calibration-verification studies. Input required includes: (i) channel width, mean depth and velocity at known distances below outfall; (ii) river discharge and pollutant background concentration; (iii) effluent concentration and flow rate; (iv)

lateral dispersion coefficient and pollutant decay rate. This model is based on the "stream tube concept" which considers the partial cumulative discharge (from a reference bank) as the lateral variable, instead of lateral distance.

MIXAPPLN - An application model using the parameters derived from MIXCALBN as inputs, along with the parameters associated with management control; i.e., design temperature and pH, effluent concentration and flow rate, and stream flow. The model outputs allowable effluent concentrations required for Ministry compliance with respect to pollutants such as chlorine, ammonia, phenol and radioactive wastes. Compliance is determined with reference to a LUZ (Limited Use Zone) of given lateral boundaries, viz., 20%, 30% and 40% of cumulative river flow from the reference bank. Also output is the downstream distance from the outfall (along the bank) at which compliance is achieved.

E. Prediction Techniques (Lakes)

The data collected can be used in the model described in: Dispersion of Effluent Plumes from Diffusers on Near-Shore Regions of the Great Lakes, Volume I, Initial Mixing Processes, Y. Hamdy (1981) and Volume II, Surface Dilution, B. Kohli (1981).

ALTERNATIVES TO CHLORINATION

1. Other Disinfection Methods

   a) Chlorination/Dechlorination - the residual chlorine toxicity can be eliminated with sulphur dioxide, bisulfite or sodium thiosulfate (dechlorination). Theoretically this technique should also greatly reduce the carcinogenic organohalides, but the cost of treatment is substantially increased. Chlorination/dechlorination is now implemented at the Milton STP.

b) Ozonation - ozonation is expensive and energy intensive. Ozone cannot be stored and it is difficult to adjust ozone levels to fluctuating treatment requirements. Ozone can rupture some large molecules in effluents into fragments more easily metabolized by micro-organisms; however, this can also lead to slime growth. In addition, ozone is a potent virucidal agent. The by-products of ozonation are relatively unknown and may also be toxic.

c) Bromine chloride - chlorobromination is more expensive than chlorine but the lethal effects to aquatic life are somewhat lower. There is some concern that chlorobromine may also produce hazardous by-products.

Further information on bromine chloride, chlorine dioxide and ultra violet disinfection are presented by Tonelli and Ho[12]. Other disinfection alternatives including gamma radiation and high-pH lime, iodine and low pH are discussed in Wastewater Disinfection in Canada[13].

All these alternatives to chlorination are still in the developmental stage and need more investigation before they can be substituted for chlorination. Any proposals to use one of these alternatives must be processed through the Pollution Control Branch in conjunction with the Environmental Approvals and Project Co-ordination Branches depending on whether proposals are for municipal or private application.

2. Other Approaches

a) Chlorination of STP effluents can be limited to those which discharge to streams directly above areas designated for recreational use; or, the approach to chlorination can be reconsidered, in view of the fact that urban and agricultural drainage are not disinfected and contain high levels of bacteria, viruses and other pathogens. In other words, the approach could be either to chlorinate all effluents that create a public health hazard, or to follow

the example of Europe, and stop or limit the practice of disinfection of wastewater[13]. However, neither of these approaches are compatible with the current disinfection policy.

b) The amount of chlorine in the effluents could be reduced if all STPs switched to DPD comparator or Amperometric techniques for measuring total residual chlorine - especially if they used continuous flow analyses to maintain the 0.5 mg/L chlorine level.

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~~TERMINAL STREAM: TRENT R.~~

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